PATENT COOPERATION TREATY

PCT

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference P211043PCT MVE	FOR FURTHER ACTION	See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)
International application No. PCT/NL2003/000766	International filing date *(day/month/year)* 04.11.2003	Priority date *(day/month/year)* 04.11.2003
International Patent Classification (IPC) or both national classification and IPC C08L101/02		
Applicant SUPRAPOLIX B.V.		

1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.

2. This REPORT consists of a total of 4 sheets, including this cover sheet.

   ☒ This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

   These annexes consist of a total of 8 sheets.

3. This report contains indications relating to the following items:

   - I ☒ Basis of the opinion
   - II ☐ Priority
   - III ☐ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
   - IV ☐ Lack of unity of invention
   - V ☒ Reasoned statement under Rule 66.2(a)(ii) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
   - VI ☐ Certain documents cited
   - VII ☐ Certain defects in the international application
   - VIII ☐ Certain observations on the international application

Date of submission of the demand	Date of completion of this report
05.07.2005	06.10.2005
Name and mailing address of the international preliminary examining authority: European Patent Office D-80298 Munich Tel. +49 89 2399 - 0 Tx: 523656 epmu d Fax: +49 89 2399 - 4465	Authorized Officer Otegui Rebollo, J Telephone No. +49 89 2399-8670

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No. PCT/NL2003/000766

I. Basis of the report

1. With regard to the **elements** of the international application *(Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report since they do not contain amendments (Rules 70.16 and 70.17))*:

Description, Pages

1-39 as published

Claims, Numbers

1-25 received on 06.05.2004 with letter of 03.05.2004

2. With regard to the **language**, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.

   These elements were available or furnished to this Authority in the following language: , which is:

   ☐ the language of a translation furnished for the purposes of the international search (under Rule 23.1(b)).

   ☐ the language of publication of the international application (under Rule 48.3(b)).

   ☐ the language of a translation furnished for the purposes of international preliminary examination (under Rule 55.2 and/or 55.3).

3. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:

   ☐ contained in the international application in written form.

   ☐ filed together with the international application in computer readable form.

   ☐ furnished subsequently to this Authority in written form.

   ☐ furnished subsequently to this Authority in computer readable form.

   ☐ The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.

   ☐ The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

4. The amendments have resulted in the cancellation of:

   ☐ the description, pages:

   ☐ the claims, Nos.:

   ☐ the drawings, sheets:

5. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)).

   (Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.)

6. Additional observations, if necessary:

V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Yes:	Claims	1-25
	No:	Claims	
Inventive step (IS)	Yes:	Claims	1-25
	No:	Claims	
Industrial applicability (IA)	Yes:	Claims	1-25
	No:	Claims	

2. Citations and explanations

see separate sheet

Re Item V

Reasoned statement with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

Reference is made to the following document:

D1: WO 98/14504 A (BEIJER FELIX HUGO ;BRUNSVELD LUCAS (NL); DSM NV (NL); MEIJER EGBER) 9 April 1998 (1998-04-09)

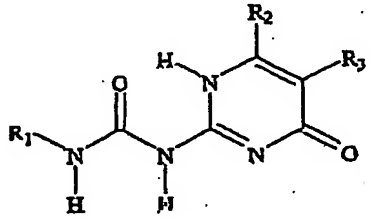
The claimed subject-matter appears to be novel and involve an inventive step (Articles 33(2,3) PCT) over the available prior art: see for instance D1 (see claim 9, where radicals R1 and R2 are linking groups), which discloses supramolecular polymer comprising quadruple hydrogen bonding units (eg ureidopyrimidone units) within the polymer backbone, but it fails to clearly suggest the claimed alternative of linking said quadruple hydrogen bonding units to the polymer backbone through invention's radical R1 with two linking groups or R1 and R3 in order to prepare further supramolecular polymers with good properties.

CLAIMS (amended May 3, 2004)

1. Supramolecular polymer comprising quadruple hydrogen bonding units within the polymer backbone, wherein at least a monomer comprising a 4H-unit is incorporated in the polymer backbone via at least two reactive groups up to four reactive groups, provided that the 4H-units are not covalently incorporated in the polymer backbone through one or more silicon-carbon bonds,
wherein the monomeric unit (a) has a structure according to formula (III) or (IV):

$$4H - (F_i)_r \quad (III)$$
$$4H^* - (F_i)_r \quad (IV)$$

wherein F_i comprises a reactive group linked to the 4H-unit or 4H*-unit; and
r is 2;
wherein the monomeric unit (a) is represented by formula (VIa):



(VIa)

wherein:

(a) the 4H-unit is connected to a reactive group (F_1) via R1 and to a reactive group (F_1) or (F_2) via R3, whereas R2 is a random side chain or a hydrogen atom, the random side chain being a linear, cyclic or branched alkyl group comprising 1 to 7 carbon atoms; or

(b) the 4H-unit is connected to two reactive groups (F_1) both via R1, whereas R2 and R3 are random side chain or hydrogen atoms, the random side chains being a linear, cyclic or branched alkyl group comprising 1 to 7 carbon atoms; or

wherein the monomeric unit (a) is represented by formula (VIIa):

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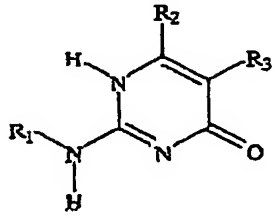


(VIIa)

wherein the 4H-unit is connected to a reactive group (F_1) via R1 and to a reactive group (F_1) or (F_2) via R3, whereas R2 is a random side chain or a hydrogen atom, the random side chain being a linear, cyclic or branched alkyl group comprising 1 to 7 carbon atoms; and

wherein R1 – R3 are selected from the group consisting of hydrogen atoms and shorter or longer chains, the longer and shorter chains being selected from the group consisting of saturated or unsaturated, branched, cyclic or linear alkyl chains, aryl chains, alkaryl chains, arylalkyl chains, ester chains or ether chains.

2. Supramolecular polymer (c) and (c') according to claim 1 comprising quadruple hydrogen bonding units in the polymer backbone, said supramolecular polymer (c) and (c') having a structure according to formula (I) or formula (II):

$$\{(a)_p\text{–}(b)_q\}_v \quad [I]$$

$$\{(a)_p\text{–}(b')_q\}_w \quad [II]$$

wherein:

(a) is a monomeric unit that comprises a (precursor of) 4H-element;

(b) is a macromonomeric unit;

(b') is a fragmented part of the original polymer (b);

(a) and (b) are connected, preferably covalently, in the polymer backbone;

p and q indicate the total number of units of (a) and (b) or (a) and (b') in the polymer backbone;

p is 1 to 100;

q is 0 to 20;

v is the number of repeating units of the connected monomeric units (a) and the connected macromonomeric units (b);

w is the number of repeating units of the connected monomeric units (a) and the connected macromonomeric units (b');

macromonomeric unit (b) has a number average molecular weight of at least about 100 to about 100000;

macromonomeric unit (b') has a number average molecular weight of at least about 50 to about 20000;

polymer (c) has a number average molecular weight of about 2000 to about 80000;.

polymer (c') has a number average molecular weight of about 2000 to about 80000;

provided that the 4H-units are not covalently incorporated in the polymer backbone through one or more silicon-carbon bonds.

3. Supramolecular polymer according to claim 1 or claim 2, wherein the macromonomeric unit (b) comprises at least two complementary reactive groups up to six complementary reactive groups.

4. Supramolecular polymer according to any one of claims 1 - 3, wherein the amount of 4H-units incorporated in the polymer backbone is about 33 to about 66 mol %, based on the total amount of moles of (a) and (b) or (a) and (b').

5. Supramolecular polymer according to any one of claims 1 - 4, wherein the macromonomeric unit (b) is represented by formula (V):

$$P\text{–}(F_i)_s \quad (V)$$

wherein:

P represents a polymer chain having a number average molecular weight of 100 to 100000;

F_i represents a complementary reactive group in the macromonomeric unit (b) that is complementary reactive with another F_i of monomeric unit (a): and

s represents the number of these groups in the macromonomer and is 0 - 6 preferably 2 - 6.

6. Supramolecular polymer according to any one of the preceding claims, wherein the macromonomeric unit (b) has a structure according to formula (VIII):

F2 - P - F2 or F1 - P - F2 (VIII)

wherein:

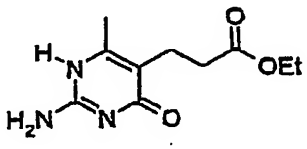
P is selected from the group consisting of polyesters, polyether, polycarbonates and hydrogenated polyolefins; and

F_1 and F_2 are independently selected from the group consisting of -OH, $-NH_2$, -NCO and $-C{=}CH_2$.

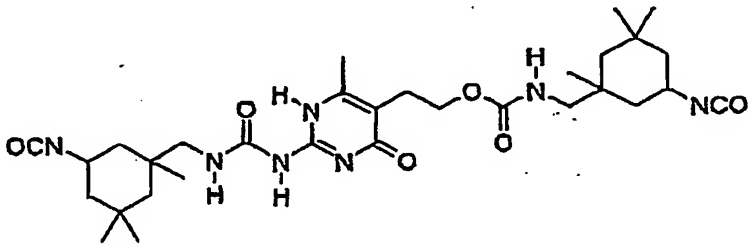
7. Supramolecular polymer according to claim 6, wherein P has a number average molecular weight of 100 to 100000.

8. Supramolecular polymer according to claim 6, wherein P has a number average molecular weight of 5000 to 100000.

9. Supramolecular polymer according to any one of claims 1 – 8, wherein the monomeric unit (a) is



10. Supramolecular polymer according to any one of claims 1 – 8, wherein the monomeric unit (a) is



11. A process for the preparation of a supramolecular polymer comprising quadruple hydrogen bonding units within the polymer backbone, wherein at least a monomer comprising a 4H-unit is incorporated in the polymer backbone via at least two reactive groups up to four reactive groups, provided that the 4H-units are not covalently incorporated in the polymer backbone through one or more silicon-carbon bonds, wherein a monomeric unit (a) having a structure according

to formulae (III) or (IV) and a macromonomeric unit (b) having a structure according to formulae (V) are reacted,

wherein the monomeric unit (a) has a structure according to formula (III) or (IV):

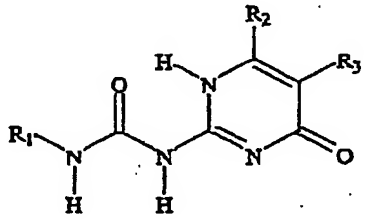
$$4H - (F_i)_r \quad (III)$$

$$4H^* - (F_i)_r \quad (IV)$$

wherein F_i comprises a reactive group linked to the 4H-unit or 4H*-unit; and

r is 2;

wherein the monomeric unit (a) is represented by formula (VIa):



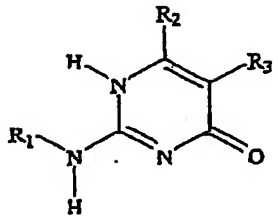
(VIa)

wherein:

(c) the 4H-unit is connected to a reactive group (F_1) via R1 and to a reactive group (F_1) or (F_2) via R3, whereas R2 is a random side chain or a hydrogen atom, the random side chain being a linear, cyclic or branched alkyl group comprising 1 to 7 carbon atoms; or

(d) the 4H-unit is connected to two reactive groups (F_i) both via R1, whereas R2 and R3 are random side chain or hydrogen atoms, the random side chains being a linear, cyclic or branched alkyl group comprising 1 to 7 carbon atoms; or

wherein the monomeric unit (a) is represented by formula (VIIa):



(VIIa)

wherein the 4H-unit is connected to a reactive group (F_1) via R1 and to a reactive group (F_1) or (F_2) via R3, whereas R2 is a random side chain or a hydrogen atom, the random side chain being a linear, cyclic or branched alkyl group comprising 1 to 7 carbon atoms; and

wherein R1 – R3 are selected from the group consisting of hydrogen atoms and shorter or longer chains, the longer and shorter chains being selected from the group consisting of saturated or unsaturated, branched, cyclic or linear alkyl chains, aryl chains, alkaryl chains, arylalkyl chains, ester chains or ether chains; and wherein the macromonomeric unit (b) is represented by formula (V):

$$P\text{–}(F_i)_s \quad (V)$$

wherein:

P represents a polymer chain having a number average molecular weight of 100 to 100000;

F_i represents a complementary reactive group in the macromonomeric unit (b) that is complementary reactive with another F_i of monomeric unit (a): and

s represents the number of these groups in the macromonomer and is 0 - 6 preferably 2 - 6.

12. Process according to claim 11, wherein the process proceeds by chain extension and wherein the following sets of monomeric unit (a) and macromonomeric unit (b) are polymerised:

(a) F_1-4H-F_1 and F_3-P-F_3;

(b) F_1-4H-F_2 and F_3-P-F_3;

(c) F_1-4H*-F_1 and F_3-P-F_3; or

(d) F_1-4H*-F_2 and F_3-P-F_3

wherein the couples F_1 - F_3 and F_2 - F_3 are complementary reactive groups.

13. Process according to claim 12, wherein the reactive groups F_i are selected from the group consisting of $-NH_2$, -NHR, -NCO, blocked -NCO, -OH, -C(O)OH, -C(O)OR wherein R is a linear or branched C_1-C_6 alkyl group, a C_6 - C_{12} arylgroup, a C_7 - C_{12} alkaryl group or a C_7 - C_{12} alkylaryl group, or R is halogen atom selected from the group consisting of Cl, Br or I.

14. Process according to any one of claims 11 - 13, wherein two or more macromonomeric units (b) having a different number average molecular weight are used.

15. Process according to any one of claims 11 - 14, wherein two or more macromonomeric units (b) having a different molecular structure are used.

16. Process according to any one of claims 11 - 15, wherein the monomeric unit (a) and/or the macromonomeric unit (b) comprises a "stopper" moiety having the formula $P\text{-}F_1$, $4H\text{-}F_1$ of $4H^*\text{-}F_1$, wherein F_1, 4H and 4H* are as defined in the preceding claims.

17. Process according to any one of claims 11 – 16, wherein branching species of monomeric unit (a) or macromonomeric unit (b) are used, said branching species having the formula $P\text{-}(F_i)_u$ or $4H\text{-}(F_i)_u$ or $4H^*\text{-}(F_i)_u$, wherein u is 3 - 6.

18. Process according to any one of claims 11 - 17, wherein the molar ratio between monomeric unit (a) and macromonomeric unit (b) is between 1:2 and 2:1.

19. Process according to claim 11, wherein the process proceeds by redistribution and wherein the following sets of monomeric unit (a) and macromonomeric unit (b) are polymerised:

(a) $F_1\text{-}4H\text{-}F_1$ and P; or

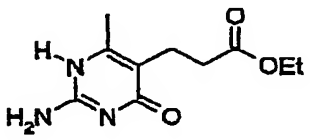
(b) $F_1\text{-}4H\text{-}F_2$ and P

wherein F_1, F_2 and P are as defined in the preceding claims.

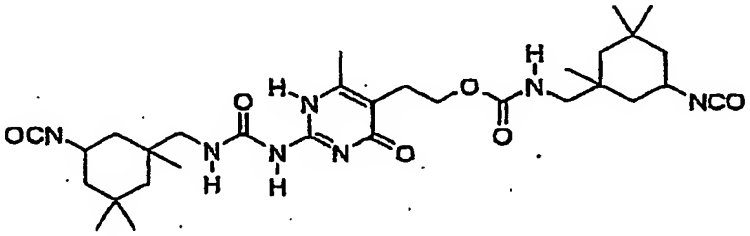
20. Process according to claim 19, wherein P has an number average molecular weight of 5000 - 100000.

21. Process according to claim 19 or claim 20, wherein the molar ratio between monomeric unit (a) and macromonomeric unit (b) is between 3:1 and 10:1.

22. Process according to any one of claims 11 – 21, wherein the monomeric unit (a) is



23. Process according to any one of claims 11 – 21, wherein the monomeric unit (a) is



24. A supramolecular polymer comprising quadruple hydrogen bonding units within the polymer backbone, wherein at least a monomer comprising a 4H-unit is incorporated in the polymer backbone via at least two reactive groups, provided that the 4H-units are not covalently incorporated in the polymer backbone through one or more silicon-carbon bonds, said supramolecular polymer being obtainable by the process according to any one of claims 11 - 23.

25. Use of a supramolecular polymer according to claims 1 - 10 or 24 in personal care applications, surface coatings, imaging technologies, biomedical applications, (thermo)reversible coatings, adhesive and sealing compositions and as thickening agents, gelling agents and binders.